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(54) Title: ALIQUOT-PACKAGE DETERGENT PRODUCT USING WATER-SOLUBLE FILM (57) Abstract An aliquot-package detergent product comprising an aliquot quantity of a detergent composition containing a nonionic surfactant packed in a water-soluble packaging film, said packaging film comprising an itaconic acid-modified polyvinyl alcohol and at least one compound selected from the group consisting of polymers and copolymers of a monomer having a carboxyl group as a constituent monomer and products of neutralization thereof, wherein the ratios of the absolute water content of the detergent composition and the amount of the nonionic surfactant contained in the detergent composition to the weight of the modified polyvinyl alcohol film fall within specific ranges, respectively.		

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SPECIFICATION

ALIUOT-PACKAGE DETERGENT PRODUCT USING WATER-SOLUBLE FILM

Background of the Invention

Field of the Invention

The present invention relates to an aliquot-package detergent product, i.e., a dispenser, comprising an aliquot quantity of a detergent packaged in a water-soluble packaging film which exhibits a high strength, which is excellent in elasticity and is free from rigidification when used for packaging a detergent therein. The packaging film provides a pleasant touch to a user who uses the packaged detergent and the breaking strength thereof lowers only a small amount during storage of the packaged detergent.

Description of the Related Art

Most of the conventional, commercially available powdered detergent products for clothes are those which comprise 100 to 200 cm³ by volume (an amount necessary for performing washing 60 to 100 times) of a detergent packaged in a paper carton which is prepared by spray drying, has a bulk density of 0.2 to 0.4 g/cm³, and is used normally in an amount of about 40 g

per 30 l of water in a unit run of washing. It has been common practice to use them either by lifting the carton itself and shaking an appropriate amount of the powdered detergent directly out of the carton into a washing machine tub or by roughly weighing a necessary amount of the detergent out of the carton with a cup or the like and throwing the weighed detergent into a washing machine tub. Recently, powdered detergents having a bulk density of 0.7 g/cm^3 or above have been developed, whereby the problem of carrying a powdered detergent or the like has been solved. However, powdered detergents having a bulk density of 0.7 g/cm^3 or above still have a handling problems in that the detergent powder scatters during the process of weighing or throwing.

In order to solve the problem of detergent powder scattering when being weighed or thrown, one-pack detergent products prepared by packaging a detergent in an amount necessary for one washing run in a water-insoluble, water-permeable or water-soluble material have been proposed. For example, Japanese Patent Publication-A Nos. 8497/1988 (published on January 14, 1988) and 12467/1988 (published on January 19, 1988) disclose certain one-pack detergent products prepared by packaging a detergent in a water-soluble material

such as a water-soluble film, specific examples of which include those prepared by packaging an aliquot quantity of a detergent having a bulk density as high as 0.5 to 1.2 g/cm³ in a water-soluble film and those prepared by packaging an aliquot quantity of a pasty detergent in a water-soluble film.

The above packaging materials have various problems and, in order to solve these problems, the present inventors made various proposals with respect to water-soluble materials, e.g., in Japanese Patent Publication-A Nos. 204254/1986 (published on September 10, 1986) and 163149/1990 (published on June 22, 1990). More specifically, the present inventors have found that a film improved in water solubility could be prepared from a composition comprising a polyvinyl alcohol having a degree of saponification of 98 mole % or above and a polyacrylic acid having a molecular weight of 2800 or below and that a polyvinyl alcohol modified with itaconic acid gives a packaging material improved in water solubility.

U. S. Patent No. 4692494 (published on September 8, 1989, Assignee: Sonenstein G G) discloses that a film made from a composition comprising a polyvinyl alcohol and a specific polyacrylic acid is improved in film strength. In fact, when a film is made from a

composition comprising a polyvinyl alcohol and a carboxylated polymer such as polyacrylic acid, the film is improved in solubility and strength. However, when an aliquot quantity of a detergent is packaged in the film to make an aliquot-package detergent product, the film tends to become rigid by the action of the detergent, so that the aliquot-package detergent product which is made with the use of such a film does not give a favorable impression to a user who desires a flexible and soft touch, excellent in elasticity. Further, when the aliquot-package detergent product is stored for a long period of time, the film strength tends to lower. These tendencies are particularly remarkable, when a polyvinyl alcohol modified with a carboxylated monomer such as itaconic acid is used [see Japanese Patent Publication-A No. 163149/1990 (published on June 22, 1990)].

Disclosure of the Invention

Summary of the Invention

The present inventors have developed an aliquot-package detergent product using a packaging film excellent in strength and water-solubility which is characterized in that the film suffers less from surface rigidification or lowering of the breaking

strength after packaging a detergent therein. As a result, the present inventors have surprisingly found that an aliquot-package detergent product comprising an aliquot quantity of a detergent packaged in a film, in which the film is excellent in elasticity and rich in flexibility and softness and does not suffer from a lowering in its breaking strength during storage of the detergent can be prepared by using a specific water-soluble film and restricting the ratios of the absolute water content of the detergent composition to be packaged and the amount of a nonionic surfactant contained in the detergent composition to the weight of the water-soluble film to be used for packaging, within specific ranges, respectively. The present invention has been accomplished on the basis of this finding.

Thus, the present invention provides an aliquot-package detergent product comprising an aliquot quantity of a detergent composition containing a nonionic surfactant packed in a water-soluble packaging film, said packaging film comprising 100 parts by weight of an itaconic acid-modified polyvinyl alcohol and 0.1 to 20 parts by weight of a compound selected from the group consisting of polymers and copolymers of a monomer having a carboxyl group as a

constituent monomer and products of neutralization thereof, wherein the amount of absolute water contained in the detergent composition ranges from 90 to 3,000 parts by weight base on 100 parts by weight of the modified polyvinyl alcohol film and the amount of the nonionic surfactant contained in the detergent composition ranges from 30 to 5,000 parts by weight based on 100 parts by weight of the modified polyvinyl alcohol film.

In other words, the present invention provides an aliquot-package detergent which is prepared by packaging a detergent composition in divided form in a modified polyvinyl alcohol film made from a composition comprising 100 parts by weight of an itaconic acid-modified polyvinyl alcohol and, incorporated therein, 0.1 to 20 parts by weight of a polymer or copolymer of a monomer having a carboxyl group or a product of neutralization thereof and which is characterized in that the ratio of the amount of absolute water contained in the detergent composition to 100 parts by weight of the modified polyvinyl alcohol film is from 90 to 3,000 parts by weight and the ratio of the nonionic surfactant contained in the detergent composition to 100 parts by weight of the modified polyvinyl alcohol film is from 30 to 5,000

parts by weight.

The aliquot-package detergent product according to the present invention is a packed detergent product comprising a prescribed amount, that is, an amount necessary for performing one washing, of a detergent composition and a water-soluble film as a package for the detergent composition, or a continuous packed detergent product comprising a continuous package made of a water-soluble film and a detergent composition packed in each bag of the continuous package in a prescribed amount.

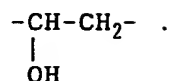
The present invention will now be described in detail.

Detailed Description of the Invention

The itaconic acid-modified polyvinyl alcohol (hereinafter, polyvinyl alcohol will be abbreviated to "PVA") to be used in the present invention is a vinyl alcohol copolymer comprising itaconic acid units and vinyl alcohol units as the essential constituent monomer units. The itaconic acid unit is a unit

represented by the formula:
$$\begin{array}{c} \text{COOH} \\ | \\ -\text{C}-\text{CH}_2- \\ | \\ \text{CH}_2\text{COOH} \end{array}$$
, while the vinyl

alcohol unit is a unit represented by the formula:



In the present invention, it is preferable to use, as the itaconic acid-modified PVA, a vinyl alcohol copolymer which is prepared by copolymerizing vinyl acetate with itaconic acid as the essential monomers and saponifying the obtained copolymer. The copolymer comprises 2 to 8 mole % of itaconic acid units, 88 to 98 mole % of vinyl alcohol units and 0 to 4 mole % of vinyl acetate units. Further, it is particularly preferable from the standpoint of balance of the properties of the film, i.e., film strength, water solubility and long-term stability under contact with an alkali, e.g., an alkaline salt, to use a copolymer comprising 3 to 6 mole % of itaconic acid units, 92 to 97 mole % of vinyl alcohol units and 0 to 2 mole % of vinyl acetate units. The vinyl acetate unit is a unit represented by the formula: $\begin{array}{c} -\text{CH}-\text{CH}_2- \\ | \\ \text{OCOCH}_3 \end{array}$,

which corresponds to an unsaponified moiety.

As described above, the itaconic acid unit content of the itaconic acid-modified PVA is suitably 2 to 8 mole %. When the itaconic acid unit content falls within this range, the resulting film not only is excellent in water solubility, but also generally

does not suffer from blocking in a rolled state. Further, it is suitable from the standpoint of solubility of the film that the vinyl acetate unit content ranges from 0 to 4 mole %.

Part or the whole of the carboxyl groups of the itaconic acid units may form a salt with a monovalent cation such as an alkali metal ion or an ammonium ion.

Although the degree of polymerization of the itaconic acid-modified PVA to be used in the present invention is not particularly limited, it is suitable with respect to film properties, particularly film strength and water solubility of the film, to use one having a degree of polymerization of 500 to 2,000.

In the present invention, only one kind of itaconic acid-modified PVA may be used, or alternatively a mixture of two or more kinds of itaconic acid-modified PVA's different from each other in composition of the constituent monomer units, molecular weight and the like may be used.

The process for preparing the itaconic acid-modified PVA to be used as the raw material of the film of the present invention is not particularly limited. The itaconic acid-modified PVA may be prepared, for example, by saponifying a copolymer prepared from vinyl acetate and itaconic acid, and the

process is disclosed, for example, in Japanese Patent Publication-A No. 91995/1978 (published on August 12, 1978).

The polymer or copolymer to be used in the present invention is one comprising a monomer unit(s) having a carboxyl group as the essential constituent monomer unit and includes homopolymers of unsaturated carboxylic acids such as acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid and allylacetic acid and copolymers of two or more of these acids, among which homopolymers and copolymers of acrylic acid, methacrylic acid, maleic acid and/or fumaric acid are preferable.

Further, a copolymer prepared with the above monomer having a carboxyl group, i.e., the above-described unsaturated carboxylic acid, and a comonomer copolymerizable therewith can be used as the copolymer of a monomer having a carboxyl group as the constituent monomer according to the present invention. Preferable examples of the comonomer include acrylonitrile, ethyl acrylate, methyl methacrylate, styrene, vinyl methyl ether, vinyl propyl ether, acrylamide, ethylene and propylene. Although the ratio of the monomer having a carboxyl group to the comonomer is not particularly limited,

the ratio thereof is within such a range as to give a water-soluble copolymer.

The neutralizing agent to be used for the neutralization of the above polymer or copolymer may be an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide, ammonia, or a monoamine such as triethanolamine. The degree of neutralization may be about 0 to 90 mole %, though it is not particularly limited.

It is preferable from the standpoint of solubility or for attaining the maximum effects according to the present invention that the homopolymer or copolymer comprising a monomer unit(s) having a carboxyl group or the product of neutralization thereof have a weight-average molecular weight of 3,000 to 100,000, particularly 5,000 to 50,000.

The homopolymer or copolymer comprising a monomer unit(s) having a carboxyl group or the product of neutralization thereof is used in an amount of 0.1 to 20 parts by weight, preferably 0.5 to 10 parts by weight, still preferably 2 to 10 parts by weight based on 100 parts by weight of the itaconic acid-modified PVA. When this amount is less than 0.1 part by weight, the film strength is not improved, whereas

when it exceeds 20 parts by weight, the film strength of the film itself is lowered and the unit-packaged detergent product packaging the detergent composition in the film becomes too poor in the elasticity of the film.

The composition to be used for the preparation of the film according to the present invention may contain a plasticizer. Although the plasticizer is not particularly limited and may be selected from among various known plasticizers, the use of a polyhydric alcohol plasticizer is preferable. Examples of a polyhydric alcohol plasticizer include ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, glycerol, trimethylolpropane, 3-methylpentane-1,3,5-triol and diglycerol, which may be used either alone or in a mixture of two or more. The plasticizer is generally used in an amount of 1 to 20 parts by weight based on 100 parts by weight of the itaconic acid-modified PVA.

Further, a surfactant may be added to the composition to be used for the preparation of the film according to the present invention for the purpose of improving the releasability of the film in the preparation thereof, the blocking resistance during

the storage of the film and the hydrophilicity in its dissolution in water. The surfactant is not particularly limited, but may be selected from among conventional anionic, nonionic and cationic surfactants and so on.

In the present invention, the process for preparing the film is not particularly limited, and thus any conventional process for the preparation of PVA films can be favorably employed. For example, the casting process which uses water as a solvent and comprises casting an aqueous solution of a film-forming composition onto a drum or belt and drying the cast composition is suitably employed. The thickness of the film is generally 10 to 150 μm , preferably 15 to 50 μm .

It is particularly effective in improving the water solubility and blocking resistance of the film that the film has an uneven surface, though the film may have a flat surface. An increase in the surface area of the film due to an uneven surface increases the contact area between the water and the film to enhance the solubility of the film in water. Further, a decrease in the contact area between the films due to an uneven surface is effective in preventing the film from blocking. It is preferable that the film

has an unevenness in a pattern of 10- to 60-mesh, in a checkered or hexagon configuration. Further, it is suitable that the film has an uneven surface so as to have an apparent thickness which is at least 1.5 times, particularly at least twice, the true thickness of the film. According to the present invention, the process for making the film uneven is not particularly limited. For example, an uneven film may be prepared by casting an aqueous solution of a film-forming composition onto a substrate having an uneven surface or by subjecting a flat film to post embossing on an embossing calender.

In the present invention, a detergent composition is packaged in the above water-soluble film so as to satisfy the requirements that the amount of absolute water originating in the detergent composition must range from 90 to 3,000 parts by weight, preferably 120 to 2,800 parts by weight, still preferably 140 to 1,200 parts by weight based on 100 parts by weight of the water-soluble film and that the amount of the nonionic surfactant contained in the detergent composition must range from 30 to 5,000 parts by weight, preferably 40 to 4,800 parts by weight, still preferably 190 to 1,050 parts by weight based on 100 parts by weight of the film. By satisfying these

requirements, the film loses its original crispness after about one hour from the packaging of the detergent composition therewith to give an aliquot-package detergent product characterized in that the film exhibits, after packaging the detergent therewith, suitable elasticity and flexibility and is soft to the touch, though the film itself has a rigid surface and is not always pleasant to the touch. Further, the breaking strength of the film is not lower, even after packaging of the detergent composition therewith, than that before the packaging.

The term "amount of absolute water" used in this specification refers to the sum total of the amount of free water contained in the detergent composition to be packaged, that of crystal water contained in the auxiliary builder salt such as crystalline aluminosilicate, amorphous hydrated aluminosilicate and sodium silicate, and that of adherent water. The amount of absolute water is determined by NMR. Specifically, it can be determined by dissolving the detergent composition to be packaged in heavy water (D_2O), determining the amount of HDO formed as represented by the following reaction formula by NMR using DMSO as the internal reference and calculating the amount of absolute water originating in the

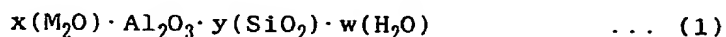
detergent composition based on the amount of H₂O thus determined:

(reaction formula) $H_2O + D_2O \rightarrow 2HDO$

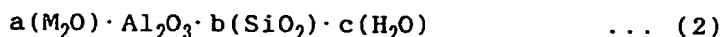
When the amount of absolute water contained in the detergent composition is less than 90 parts by weight based on 100 parts by weight of the film, the film is not at all improved in its rigidity property, even after the packaging of the detergent composition therewith, whereas when it exceeds 3,000 parts by weight, the film strength is lowered. The detergent composition to be packaged is preferably one containing absolute water in an amount of 3 to 15% by weight, still preferably 5 to 14% by weight based on the entire amount of the detergent composition. When a detergent composition containing absolute water in an amount exceeding 15% by weight is packaged in the film, the film has a tendency to become rigid after packaging the detergent composition therein. Furthermore, during the storage of the resulting packaged detergent, the breaking strength of the film tends to become lower, the film sometimes adheres to the detergent composition packaged therein, and the detergent composition can be put in danger of solidification.

The detergent composition according to the

present invention may be any one so far as it contains a nonionic surfactant and can satisfy the above requirements with respect to the amounts of absolute water and nonionic surfactant contained therein when it is packaged in the above water-soluble film. The detergent composition generally contains, in addition to the nonionic surfactant, at least one surfactant selected from the group consisting of an anionic surfactant, a cationic surfactant and an amphoteric surfactant, at least one aluminosilicate selected from the group consisting of crystalline aluminosilicates represented by the formula (1) and amorphous aluminosilicates represented by the formula (2), at least one inorganic salt selected from among carbonates, sulfates and silicates, and/or at least one auxiliary detergent builder salt selected from among sodium pyrophosphate, sodium tripolyphosphate, sodium citrate and sodium nitrilotriacetate:



wherein M represents an alkali metal atom; and x, y and w each represent the number of molecules of the respective component and satisfy the relationships: $0.7 \leq x \leq 1.5$ and $0.8 \leq y \leq 6$, with w being an arbitrary positive number,



wherein M represents an alkali metal atom; and a, b and c each represent the number of molecules of the respective component and satisfy the relationships: $0.7 \leq a \leq 2.0$ and $0.8 \leq b \leq 6$, with c being an arbitrary positive number.

Examples of the nonionic surfactant to be contained in the detergent composition according to the present invention include polyoxyethylene alkyl ether, polyoxlethylene nonylphenyl ether, fatty acid esters of polyoxyethylene sorbitan, and fatty acid esters of polyoxyethylene sorbitol. In the present invention, it is particularly desirable to use a polyoxyethylene alkyl ether prepared by the addition reaction of a straight-chain or branched, saturated or unsaturated alcohol having 12 to 18, preferably 12 to 16 (an average value) carbon atoms with 1 to 20, preferably 3 to 15 (an average value) ethylene oxide molecules (hereinafter, ethylene oxide will be abbreviated to "EO"), or a polyoxyethylene nonylphenyl ether wherein the polyoxyethylene moiety is derived from 1 to 20, preferably 6 to 12 EO molecules (an average value).

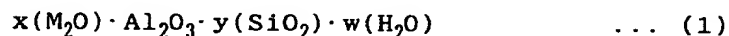
Although a nonionic surfactant may be contained in the detergent composition according to the present invention in such an amount that the weight ratio of

the nonionic surfactant to the water-soluble film falls within the above range, it is desirable that the nonionic surfactant be contained in the detergent composition in an amount of 1 to 25% by weight, more desirably 2 to 24% by weight, most desirably 15 to 24% by weight. When a packaged detergent is prepared by packaging an aliquot quantity of a detergent composition containing 15 to 24% by weight of a nonionic surfactant in the film, the breaking strength of the film increases during the storage of the packaged detergent.

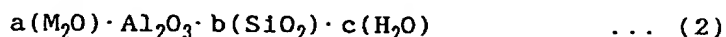
According to the present invention, one or more members selected from among conventional anionic, cationic and amphoteric surfactants for detergent compositions may be used in addition to the above nonionic surfactant and the amount thereof to be added may be about 5 to 40% by weight based on the entire amount of the detergent composition. Further, it is preferable that the weight ratio of the nonionic surfactant to the other surfactant(s) be 3 or above. When a detergent composition containing a nonionic surfactant alone or one containing a nonionic surfactant and a cationic surfactant in a weight ratio of the former to the latter of 3 or above is packaged in the film according to the present invention, the

breaking strength of the film is enhanced during the storage of the packaged detergent. Accordingly, the use of such a detergent composition is particularly preferable.

The detergent composition to be packaged may contain at least one aluminosilicate selected from the group consisting of crystalline aluminosilicates represented by the formula (1) and amorphous aluminosilicates represented by the formula (2) in an amount of 10 to 60% by weight based on the entire amount of the detergent composition as a water softener or detergent builder:



wherein M represents an alkali metal atom; and x, y and w each represent the number of molecules of the respective component and satisfy the relationships: $0.7 \leq x \leq 1.5$ and $0.8 \leq y \leq 6$, with w being an arbitrary positive number.



wherein M represents an alkali metal atom; and a, b and c each represent the number of molecules of the respective component and satisfy the relationships: $0.7 \leq a \leq 2.0$ and $0.8 \leq b \leq 6$, with c being an arbitrary positive number.

Of course, these crystalline and amorphous

aluminosilicates can also be used to cover the surfaces of the detergent particles as a surface modifier.

Further, the detergent composition to be packaged may contain at least one inorganic salt selected from among carbonates, sulfates and silicates in an amount of 5 to 60% by weight based on the whole amount of the detergent composition as a detergent builder and/or at least one sodium salt selected from among sodium phosphates (such as sodium pyrophosphate and sodium tripolyphosphate), sodium citrate and sodium nitrilotriacetate in an amount of 1 to 20% by weight based on the entire amount of the composition as another water softener (or detergent builder).

Furthermore, the detergent composition to be packaged according to the present invention may contain, in addition to the above components, other conventional additive(s) for detergents as needed. Examples of conventional additives include a small amount of an anti-redeposition agent such as polyacrylic acid or carboxymethylcellulose; an enzyme such as cellulase, protease, sabinase or lipase; a reducing agent such as a sulfite; a bleaching agent such as sodium percarbonate or sodium perborate; a bleach activator; a fluorescent dye; and a fragrance.

The detergent composition to be packaged according to the present invention can be prepared by any conventional process and examples of the process include one which comprises intimately blending essential and arbitrary components on a kneader or the like and disintegrating the obtained intimate mixture, and one which comprises preparing a slurry containing part or the whole of the constituent components of the detergent composition, spray-drying the slurry and granulating the obtained powder.

Although the bulk density of the detergent composition to be used in the present invention may be generally 0.3 to 1 g/cm³, the use of a detergent composition having a bulk density of as high as 0.5 g/cm³ or above is preferable from the standpoint of handleability.

According to the present invention, the weight ratio of the water-soluble film to the detergent composition to be packaged therein may generally lie between 0.5 : 99.5 and 3.0 : 97.0.

The process for the production of the aliquot-package detergent product of the present invention, i.e., the process for packaging an aliquot-quantity of a detergent composition in the film is not particularly limited. Generally, the aliquot package

detergent product of the present invention is produced by heat sealing the film on an automatic packaging machine having a three-way sealing system or by bonding the film with an adhesive at the fringe portions of the bags, thereby making bags of the film; packing a detergent composition into each bag; closing the opening of the bag by heat sealing or with an adhesive, and cutting off the bags from each other as needed. The area of the heat-seal or bonded portion may generally occupy at most 25% of that of the package.

Example

The present invention will now be described by referring to the following Examples, although the present invention is not limited thereby. Unless otherwise stated, all parts and percentages are by weight.

Preparative Example <preparation of itaconic acid-modified PVA>

350 parts of vinyl acetate, 40 parts of methanol and 2 parts of a 25% solution of itaconic acid in methanol were fed into a polymerizer fitted with a temperature control unit, a stirrer, a water condenser, a dropping funnel, a thermometer and a nitrogen gas inlet tube. The contents were heated to

60°C under stirring, followed by the purging of the system with nitrogen. 0.25 part of 2,2'-azobis-isobutyronitrile was added into the polymerizer together with 20 parts of methanol to initiate copolymerization. 24.8 parts of a 25% solution of itaconic acid in methanol was uniformly added into the polymerizer in 3.5 hours from the initiation of the copolymerization, while suitably monitoring the solid content of the copolymerization system. The copolymerization was terminated by the addition of thiourea. Methanol vapor was blown into the obtained copolymer paste to resolve unreacted vinyl acetate, followed by the addition of methanol to prepare a solution of the copolymer in methanol (final copolymer content: 30%). 33 parts of a solution of sodium hydroxide in methanol (NaOH concentration: 10%) was added to 200 parts of the solution of the copolymer in methanol at 40°C under stirring to saponify the copolymer, thus giving a gel. This gel was pulverized on a mixer, washed with methanol, and dried at 100°C for 2 hours to give an itaconic acid-modified PVA as a white powder (hereinafter, this itaconic acid-modified PVA is referred to as "PVA-1").

Further, the same procedure as that of PVA-1 was repeated except that the composition of monomers was

changed, by which PVA-2 was obtained. The results obtained by conducting analyses for the compositions of the constituent monomers of PVA-1 and PVA-2 are shown in Table 1.

Since "PVA 217" (a product of Kuraray Co., Ltd.) was used as a comparative PVA in the following Examples, the result obtained by conducting analysis for the composition of the constituent monomers thereof was also shown in Table 1 as PVA-3.

Table 1

	PVA-1	PVA-2	PVA-3
itaconic acid unit content (mole %)	3.1	4.8	—
vinyl alcohol unit content (mole %)	95.0	94.3	88.5
vinyl acetate unit content (mole %)	1.9	0.9	11.5

Example 1

- (1) preparation of film and evaluation of film properties

100 parts of PVA-1 was dissolved in 570 parts of water, followed by the addition of 5 parts of a polyacrylic acid (hereinafter sometimes abbreviated to "PAA") having a weight-average molecular weight of

8,000, 10 parts of glycerol and 0.3 part of Emulgen 108 [a product of Kao Corporation, polyoxyethylene (6 mol) lauryl ether]. The obtained aqueous solution was cast onto a rotating drum at a surface temperature of 75°C to form a film having a dry thickness of 25.5 μm (this film will be referred to as "Film no. 1"). This film was evaluated for various properties by the methods which will be described below.

Further, several films were prepared and evaluated in the same manner as that described above except that various PVAs and various (co)polymers of a monomer having a carboxyl group or products of neutralization thereof were used instead of the PVA-1 and the polyacrylic acid, respectively.

The results are given in Table 2.

[Evaluation methods for film properties]

- film strength

A dumbbell specimen (JIS no.2, length: 100mm) was die cut from each film. The specimen was stored under the conditions of 25°C and 65%RH for 48 hours and then subjected to the tensile test with an autographic tensilometer (mfd. by Shimadzu Corporation) to determine the breaking strength and elongation at breakage. The tensile test was conducted by holding the specimen at portions of 25mm from the top of the

specimen and 25mm from the bottom of the specimen and stretching the specimen under the conditions of 25°C and 65%RH.

- solubility in cold water

Each film was cut into a piece (4 cm × 4 cm) and this piece was dropped into 1,000 ml of city water at 10°C under stirring to determine the time which has elapsed until the complete dissolution of the piece.

Table 2

Film no.	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9
kind of PVA	PVA-1	PVA-1	PVA-1	PVA-2	PVA-1	PVA-1	PVA-1	PVA-3	PVA-1
kind of (co)polymer of a monomer having a carboxyl group *1	PAA	PAA	PAA	PAA	PAA/PMMA	PAA/maleic acid	PAA/PMMA	PAA	-
kind of neutralizing agent *2	-	NaOH	NaOH	NaOH	-	-	NaOH	-	-
degree of neutralization *2 (mole %)	-	30%	30%	30%	-	-	30%	-	-
amt. of (co)polymer of a monomer having a carboxyl group or product of neutralization thereof *3	5	5	10	5	5	5	5	5	-
breaking strength (kgf/mm ²)	3.9	3.8	3.6	3.9	4.0	3.9	3.8	4.2	3.8
elongation at breakage (%)	220	230	240	220	225	230	235	230	220
water solubility (sec)	35	32	30	33	35	33	30	50 or above	35

note) *1 PAA: polyacrylic acid, weight-average molecular weight: 8,000

PAA/PMMA: copolymer of acrylic acid (80%) and methacrylic acid (20%), weight-average molecular weight: 10,000

PAA/maleic acid: copolymer of acrylic acid (70%) and maleic acid (30%), weight-average molecular weight: 50,000

*2 kind of neutralizing agent and degree of neutralization in a case using a product of neutralization of a (co)polymer of a monomer having a carboxyl group

*3 weight per 100 part by weight of PVA

- (2) production of aliquot-package detergent and evaluation of film properties

Spray-dried powders were prepared by the use of the components of each detergent composition listed in Tables 3 or 4 except nonionic surfactant and components for which post-addition is preferable (such as enzyme, fragrance and part (10 % by weight) of zeolite or a porous silica blended), and fed into an agitating-tumbling granulator (Lödige mixer), followed by the gradual addition of a nonionic surfactant in an amount specified in Tables 3 or 4 and then an enzyme, a fragrance and a small amount of type 4A zeolite, whereby final detergent compositions each having a formulation specified in Tables 3 or 4 were prepared.

This detergent composition was packaged in an aliquot quantity in the water-soluble film prepared in the above item (1) to give an aliquot-package detergent product. The packaging was conducted by feeding the film prepared in the above item (1) into an automatic packaging machine having a three-way sealing system "K-10" (mfd. by Topack Co., Ltd.) to make continuous bags, packing each of the detergent compositions specified in Tables 3 and 4 into the bags and heat-sealing the tops of the bags. Each bag portion had a length of 10 cm, a width of 6 cm and a

heat sealed fringe width of 0.5 cm (weight of the bag: 0.4 g).

The aliquot-package detergent products thus produced were stored under the conditions of 23°C and 55%RH for one week and thereafter the films of the packages with the exception of their respective sealed parts were cut out. The obtained film pieces were subjected to the tensile test with an autographic tensilometer (mfd. by Shimadzu Corporation) to determine the breaking strength.

Meanwhile, the absolute water content of each detergent composition was determined as follows: 1 g of a sample was accurately weighed into a centrifugal tube, followed by the addition of 10 g of heavy water (D_2O) (containing dimethyl sulfoxide as internal reference). The centrifugal tube was hermetically capped and the contents were fully agitated for about 5 minutes. The resulting mixture was centrifuged to recover a supernatant, which was analyzed by NMR (60 MHz) to calculate the absolute water content from the peak heights of HDO and DMSO. This procedure was repeated twice for each sample and the average of the two values was regarded as the absolute water content.

The results are given in Tables 3 and 4.

Among the detergent compositions listed in Tables

3 and 4, those numbered with a figure enclosed with a circle are comparative.

Table 3

Components (% by wt.)		Detergent composn. no.							
		1	2	0	4	5	0		
sodium linear alkyl(C ₁₂₋₁₈)benzenesulfonate		20	20	20	20			25	
sodium alkyl(C ₁₂₋₁₈)sulfate		8	8	8	8			8	
soap [sodium salt of beef tallow(C ₁₈₋₂₄)fatty acid]		3	3	3	3			3	
polyoxyethylene alkyl ether nonionic surfactant #1		4	4		4	20		4	
polyoxyethylene alkyl ether nonionic surfactant #2									
type 4A zeolite		25	25	25	10	23		25	
sodium citrate					10				
amorphous silicon derivative #3					5	10			
Tokusil NR #4						10			
No. 2 sodium silicate		10	10	10	5			10	
sodium carbonate		4	4	0	10	20		4	
potassium carbonate		5	5	5	4			5	
sodium sulfate		3	3	5	4	5		3	
polyethylene glycol (MW = 15,000)		2	2	2	2	2		2	
polysodium acrylate (MW = 10,000)		1.5	1.5	1.5	1.5	1.5		1.5	
enzyme #5		2	2	2	2	2		2	
fluorescent dye and fragrance #6		1.5	1.5	1.5	1.5	1.5		1.5	
water		5	5	5	4	5		5	
total amount		100	100	100	100	100		100	
absolute water content of detergent composn. (% by wt.)		12	12	12	7	9.5		12	
nonionic surfactant content of detergent composn. (% by wt.)		4	4	0	4	20		4	
film no.		2	2	3	3	2		0	
film/detergent (wt. ratio)		1/99	2/98	4/90	2/98	2/98		2/98	
wt. ratio of absolute water to film #7		1188	588	288	343	405.5		588	
wt. ratio of nonionic surfactant to film #8		390	190	0	190	980		190	
breaking strength of film after one-week storage (Kgf/mm ²)		3.8	3.8	3.0	3.7	4.4		2.2	

Table 4

Components (% by wt.)		Detergent composn. no.										
sodium linear alkyl(C ₁₂₋₁₄)benzenesulfonate		5										
sodium alkyl(C ₁₂₋₁₅)sulfate												
soap [sodium salt of beef tallow(C ₁₂₋₁₅)fatty acid]												
polyoxyethylene alkyl ether nonionic surfactant #1		20	21	20	20							20
polyoxyethylene alkyl ether nonionic surfactant #2											20	
type 4A zeolite		15								25	23	25
sodium citrate		7	15	10								
amorphous silica derivative #3		10									10	
Tokusil NR #4		10	15	20	10	10	10	10	10	10	10	10
No. 2 sodium silicate												
sodium carbonate		10	20	25	10	20	10	20	10			
potassium carbonate												
sodium sulfate		5	20	20	8	5	8					
polyethylene glycol (MW = 15,000)		2	2		2	2	2					
polysodium acrylate (MW = 10,000)		1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
enzyme #5		2	2	2	2	2	2	2	2	2	2	2
fluorescent dye and fragrance #6		1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
water		5	2	0	10	5	10					
total amount		100	100	100	100	100	100	100	100	100	100	100
absolute water content of detergent composn. (% by wt.)		8	3	1	17	0.5	17					
nonionic surfactant content of detergent composn. (% by wt.)		20	21	20	20	20	20	20	20	20	20	20
film no.		7	3	3	7	2	2	2	2	2	2	2
film/detergent (wt. ratio)		2/98	2/98	2/98	2/98	2/98	2/98	2/98	2/98	2/98	2/98	2/98
wt. ratio of absolute water to film #7		392	147	49	833	465.5	833					
wt. ratio of nonionic surfactant to film #8		980	1029	980	980	980	980	980	980	980	980	980
breaking strength of film after one-week storage (Kgf/mm ²)		4.5	4.2	3.5	4.0	4.3	4.0	4.3	4.0	4.3	4.0	3.0

note)

- *1 one in which the alkyl moiety has 12 carbon atoms on an average and the polyoxyethylene moiety is derived from 6 EO on an average and which comprises at least 80% of those having an alkyl(C₁₂₋₁₆) moiety and a polyoxyethylene moiety derived from 3 to 15 EO.
- *2 one in which the alkyl moiety has 14 carbon atoms on an average and the polyoxyethylene moiety is derived from 12 EO on an average and which comprises at least 75% of those having an alkyl (C₁₂₋₁₆) moiety and a polyoxyethylene moiety derived from 3 to 15 EO.
- *3 porous silica having a pore volume of 310 cm³/100 g, a specific surface area of 153 m²/g and an oil absorption of 245 ml/100 g.
- *4 porous silica, a product of Tokuyama Soda Co. Ltd.
- *5 cellulase/protease (1 : 2, by weight) mixture
- *6 addition of 0.3% by weight of a DM-type fluorescent dye (a product of Sumitomo Chemical Co., Ltd.), 0.2% by weight of Tinopal CBS (a product of Ciba-Geigy (Japan) Ltd.) and 1% by weight of a conventional fragrance for detergent.
- *7 amount (parts by weight) of absolute water

contained in detergent composition per 100 parts
by weight of the film used.

- *8 amount (parts by weight) of nonionic surfactant
contained in detergent composition per 100 parts
by weight of the film used.

CLAIMS

1. An aliquot-package detergent product comprising an aliquot quantity of a detergent composition containing a nonionic surfactant packed in a water-soluble packaging film, said packaging film comprising 100 parts by weight of an itaconic acid-modified polyvinyl alcohol and 0.1 to 20 parts by weight of a compound selected from the group consisting of polymers and copolymers of a monomer having a carboxyl group as a constituent monomer and products of neutralization thereof, wherein the amount of absolute water contained in the detergent composition ranges from 90 to 3,000 parts by weight base on 100 parts by weight of the modified polyvinyl alcohol film and the amount of the nonionic surfactant contained in the detergent composition ranges from 30 to 5,000 parts by weight based on 100 parts by weight of the modified polyvinyl alcohol film.

2. The aliquot-package detergent product as set forth in claim 1, wherein the polymers and copolymers of a monomer having a carboxyl group as a constituent monomer and products of neutralization thereof have a weight-average molecular weight of 3,000 to 100,000.

3. The aliquot-package detergent product as set

forth in claim 1, wherein the itaconic acid-modified polyvinyl alcohol is a polyvinyl alcohol copolymer which is prepared by copolymerizing vinyl acetate with itaconic acid as essential monomers and saponifying the obtained copolymer and which comprises 2 to 8 mole % of itaconic acid units, 88 to 98 mole % of vinyl alcohol units and 0 to 4 mole % of vinyl acetate units.

4. The aliquot-package detergent product as set forth in claim 1, wherein the modified polyvinyl alcohol film has a film thickness of 10 to 150 μm .

5. The aliquot-package detergent product as set forth in claim 1, wherein the monomer having a carboxyl group is at least one member selected from the group consisting of acrylic acid, methacrylic acid, maleic acid, fumaric acid and itaconic acid.

6. The aliquot-package detergent product as set forth in claim 1, wherein the absolute water content of the detergent composition is 3 to 15% by weight.

7. The aliquot-package detergent product as set forth in claim 1, wherein the nonionic surfactant content of the detergent composition is 1 to 25% by weight.

8. The aliquot-package detergent product as set forth in claim 1, wherein the nonionic surfactant

content of the detergent composition is 15 to 24% by weight.

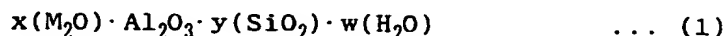
9. The aliquot-package detergent product as set forth in claim 1, wherein the nonionic surfactant is a polyoxyethylene alkyl ether in which the alkyl moiety has 12 to 18 carbon atoms on an average and the polyoxyethylene moiety is derived from 1 to 20 ethylene oxide(s) on an average and/or a polyoxyethylene nonylphenyl ether in which the polyoxyethylene moiety is derived from 1 to 20 ethylene oxide(s) on an average.

10. The aliquot-package detergent product as set forth in claim 1, wherein the detergent composition further contains at least one surfactant selected from the group consisting of an anionic surfactant, a cationic surfactant and an amphoteric surfactant, in an amount of 5 to 40% by weight.

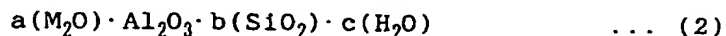
11. The aliquot-package detergent product as set forth in claim 10, wherein the detergent composition contains a nonionic surfactant and at least one surfactant selected from the group consisting of an anionic surfactant, a cationic surfactant and an amphoteric surfactant at a weight ratio of the former to the latter of 3 or above.

12. The aliquot-package detergent product as set

forth in claim 1, wherein the detergent composition further contains at least one member selected from the group consisting of crystalline aluminosilicates represented by the formula (1) and amorphous aluminosilicates represented by the formula (2) in an amount of 10 to 60% by weight:



wherein M represents an alkali metal atom; and x, y and w each represent the number of molecules of the respective component and satisfy the relationships: $0.7 \leq x \leq 1.5$ and $0.8 \leq y \leq 6$, with w being an arbitrary positive number,



wherein M represents an alkali metal atom; and a, b and c each represent the number of molecules of the respective component and satisfy the relationships: $0.7 \leq a \leq 2.0$ and $0.8 \leq b \leq 6$, with c being an arbitrary positive number.

13. The aliquot-package detergent product as set forth in claim 1, wherein the detergent composition further contains at least one inorganic salt selected from the group consisting of carbonates, sulfates and silicates in an amount of 5 to 60% by weight.

14. The aliquot-package detergent product as set forth in claim 1, wherein the detergent composition

further contains at least one auxiliary detergent builder salt selected from the group consisting of sodium pyrophosphate, sodium tripolyphosphate, sodium citrate and sodium nitrilotriacetate in an amount of 1 to 20% by weight.

15. The aliquot-package detergent product as set forth in claim 1, which is in a form of a one-pack detergent.

16. The aliquot-package detergent product as set forth in claim 1, which comprises a plural number of bags as a package made of the water-soluble film and the detergent composition packed in the each bag, said bags are connected with each other.

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MC : C11D- 17/04
ET : ALIQUOT-PACKAGE DETERGENT PRODUCT USING WATER-SOLUBLE FILM
FT : PRODUIT DETERGENT A CONDITIONNEMENT ALIQUOTE UTILISANT UN FILM HYDROSOLUBLE
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